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(54) **Integrated thermoplastic resin/silicone rubber articles and methods of making them**

Verbundgegenstände aus einem thermoplastischen Harz und einem Silikonkautschuk und Verfahren zu deren Herstellung

Objets intégrés en résine thermoplastique et caoutchouc de silicone et procédé pour leur fabrication

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(56) References cited:
EP-A- 0 143 994
EP-A- 0 178 896
EP-A- 0 249 336
EP-A- 0 276 790
EP-A- 0 314 847

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Description

This invention relates to integrated thermoplastic resin/silicone rubber articles, more particularly, integrated articles comprising a moulding of a thermoplastic resin, such as polyethylene, polypropylene or nylon resin, with a silicone rubber layer integrally joined thereto. It relates also to methods for preparing these.

It is quite difficult to join silicone rubber firmly to polyolefin resins such as polyethylene, polypropylene and fluorine resins. Silicone rubber can be attached to nylon resins and polycarbonate resins by applying a primer to them before the silicone rubber, or by moderately heat-curing uncured silicone rubber over a relatively long period, but the bonding force is low.

Silicone rubbers are now finding widespread use in electric, automobile and other applications, being recognized as reliable with respect to heat resistance, weather resistance and electrical properties. There is therefore a need for a method capable of firmly joining silicone rubber to thermoplastic resin to form an integrated article.

Several proposals have been made. EP-A-143994 and its equivalent JP-A-178046/1985 disclose adding an organohydrogenpolysiloxane containing more than 30 mol% of organohydrogensiloxane unit to an olefin resin, in order to bond silicone rubber to the olefin resin. Since this organohydrogenpolysiloxane has a relatively long polysiloxane chain and is poorly compatible with thermoplastic resin, it can give rise to undesired phenomena such as separation and substantially affect the mechanical properties of a moulded thermoplastic resin, in particular causing a loss of modulus.

JP-A-52/090079 discloses a polyethylene composition cross-linkable by condensation reaction, used for coating electric wires. The polyethylene is rendered cross-linkable by the grafting of silicon monomers, among which only vinyltrimethoxysilane and vinyltrioxysilane are exemplified, at elevated temperature in the presence of dicumyl peroxide initiator.

EP-A-276790 and JP-A-183843/1988 disclose that silicone rubber can be bonded to an olefin resin by adding to the olefin resin a silicon compound containing an organic group having at least one aliphatic unsaturated bond, and having at least one hydrolysable group attached to silicon atom.

This silicon compound is free of the above-mentioned drawbacks of JP-A 178046/1985, but is less reactive with silicone rubbers, especially addition type silicone rubbers so that no satisfactory adhesion is obtained unless a primer is used. There is commercially available a silane-crosslinked polyethylene which falls within this concept. Our attempt to cure addition type silicone rubber directly to the silane-crosslinked polyethylene failed to achieve a satisfactory bond.

It would be desirable to overcome at least partially the above-mentioned drawbacks of the prior art and to provide an integrated article in which a thermoplastic resin and a silicone rubber are firmly joined so that both the components may exert their own effects. Another object is to provide a method for preparing the integrated article.

We have found that when a thermoplastic resin is modified with certain silicon-containing compounds, the thermoplastic resin is moulded into a shape, an uncured silicone rubber is contacted with the moulded thermoplastic resin and then addition-cured against the thermoplastic resin at a temperature below the softening point of the thermoplastic resin, the silicone rubber can be firmly joined to the thermoplastic resin. The techniques described herein can avoid problems arising with the above-referred organohydrogenpolysiloxane of EP-A-143994 containing more than 30 mol% of an organohydrosiloxane unit.

Specifically, in a first aspect the invention provides an integrated thermoplastic resin/silicone rubber article comprising

(a) a moulded shape of a thermoplastic resin which has been modified by melt-mixing with a compatible monomeric or polymeric silicon-containing compound having per molecule at least one aliphatic unsaturated group and at least one $-SiR_2H$ or $-SiRH_2$ group, R being C_{1-10} hydrocarbon with optional substitution; and
(b) a silicone rubber layer formed by curing, at a temperature below the softening point of the thermoplastic resin, an addition-curable silicone rubber composition in contact with the moulded shape.

In a second aspect the invention provides a method of making a thermoplastic resin/silicone rubber integrated article comprising the steps of

(a) modifying a thermoplastic resin by melt-mixing and heating with it a compatible monomeric or polymeric silicon-containing compound having per molecule at least one aliphatic unsaturated group and at least one - SiR_2H or $SiRH_2$ group, R being C_{1-10} hydrocarbon with optional substitution;
(b) moulding the modified thermoplastic resin into a shape;
(c) contacting an uncured addition-curable silicone rubber composition with the moulded thermoplastic resin, and
(d) addition-curing the silicone rubber onto the thermoplastic resin at a temperature below the softening point of the thermoplastic resin.

DETAILED DESCRIPTION

The integrated article of the present invention comprises a silicone rubber layer integrally joined to a moulded shape of a thermoplastic resin. The thermoplastic resin has been modified with a silicon-containing compound as defined above.

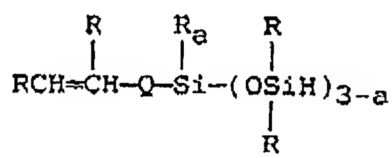
The thermoplastic resins to which the invention is applicable include, for example, polyethylene, polypropylene, fluorocarbon, polyamide, and polycarbonate resins although the invention is not limited to these resins.

The silicon-containing compound with which the thermoplastic resin is modified is not particularly limited as long as it is compatible with the resin, has an aliphatic unsaturated group and hydrogen atom directly attached to a silicon atom as represented by $-SiR_2H$ or $-SiRH_2$ wherein R is a monovalent substituted or unsubstituted hydrocarbon group having 1 to 10 carbon atoms, preferably 1 to 8 carbon atoms, for example alkyl groups such as methyl, ethyl, propyl, butyl, hexyl and cyclohexyl groups; aryl groups such as phenyl, tolyl, and naphthyl groups; aralkyl groups such as benzyl and phenylethyl groups; and halosubstituted alkyl groups such as chloromethyl and trifluoropropyl groups.

The aliphatic unsaturated group in the silicon-containing compound is important when the compound is a monomer or has a relatively low molecular weight. The aliphatic unsaturated groups include alkenyl groups such as vinyl, allyl, propenyl, and butenyl groups; and acryloxypropyl, methacryloxypropyl, cyclohexenyl, cyclopentadienyl, ethynyl, and cinnamylpropyl groups. These aliphatic unsaturated groups are organic groups capable of radical reaction with free radicals created in the thermoplastic resin. In the silicon-containing compound the hydrogen atom attached to a silicon atom can also play the role of an organic group capable of radical reaction with free radicals created in the thermoplastic resin.

The silicon-containing compound may be either a monomer or a polymer.

Monomeric silicon-containing compounds of the following formula have been found suitable:



wherein Q is a divalent group having 1 to 10 carbon atoms, and may be unsubstituted or substituted hydrocarbon group or COOR' (in which R' is an unsubstituted or substituted divalent hydrocarbon group such as an alkylene group or arylene group). Groups R (identical or different) may be hydrogen, or an unsubstituted or substituted monovalent hydrocarbon group having 1 to 8 carbon atoms such as an alkyl group or aryl group. a is 0, 1 or 2.

More specific examples are:

$$\mathrm{CH_2{=}CHCOOCH_2CH_2CH_2Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}H)_3}$$

$$\mathrm{CH_2{=}CHC_6H_4Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}H)_3}$$

$$\mathrm{C_6H_5CH{=}CHCOOCH_2CH_2CH_2Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}H)_3}$$

$$\mathrm{CH_2{=}CHCH(CH_3)Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}H)_3}$$

$$\mathrm{CH_2{=}C(CH_3)COOCH_2CH_2CH_2Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}H)_3}$$

Also useful are polymers of these silicon-containing compounds and binary or more copolymers of these silicon-containing compounds with other polymerizable monomers such as alkyl acrylates, styrene, maleic anhydride, vinyl ether, vinyl acetate, and vinyl silane. For brevity's sake, both the monomers and polymers are simply referred to as "silicon-containing compounds", hereinafter.

Preferably the silicon-containing compound is blended in amounts of about 0.1 to about 50 parts, more preferably about 0.5 to about 10 parts by weight per 100 parts by weight of the thermoplastic resin. Less than 0.1 part by weight of the compound would be too small to modify the thermoplastic resin so as to firmly bond with silicone rubber whereas more than 50 parts by weight of the compound would adversely affect the physical properties of the thermoplastic resin.

The thermoplastic resin is modified with the silicon-containing compound by heating and mixing the components. This hot mixing may be carried out by mixing and dispersing the silicon-containing compound in the thermoplastic resin at a temperature above the softening point of the thermoplastic resin. The mixing apparatus is not particularly limited provided that the components are uniformly mixed. For example, kneaders, Banbury mixers screw extruders or the like may be used. In particular, the thermoplastic resin and a silicon-containing compound may be mixed by charging the mixer with the resin in particulate form and the compound in solid form at the same time and mixing the components while heating, or by previously heating the resin in the mixer to a molten state, then adding the compound to the mixer, and mixing the components. An alternative is screw-assisted melt mixing as found in injection molding and extrusion molding.

During this hot mixing, it is recommended to use a free radical-releasing compound in combination where the silicon-containing compound used is a monomer. A variety of free radical-releasing compounds are known although preferred examples include organic peroxides such as benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, t-butyl peracetate, 2,5-dimethyl-2,5-di-t-butyl peroxyhexane, 2,5-dimethyl-2,5-di-t-butyl peroxyhexine, and t-butyl perbenzoate; azo compounds such as azobisisobutyronitrile and dimethylazodiisobutylate; -Si-Si- compounds such as disilane and polysilane; and transition metal compounds such as cerium oxide and cerium hydroxide.

with the organic peroxides being preferred for availability and ease of handling. Where such a free radical-releasing compound is used, it is sometimes advantageous to heat the system to a sufficient temperature for free radicals to release. More particularly, a temperature above the softening point of the thermoplastic resin is chosen for efficient mixing and a temperature between 100°C and 200°C is chosen for efficient release of free radicals. Thus treatment at a temperature between 100°C and 200°C and above the softening point of the thermoplastic resin is recommended. The free radical-releasing compound is preferably blended in amounts of about 0.01 to about 2 parts, more preferably about 0.05 to about 0.5 parts by weight per 100 parts by weight of the thermoplastic resin.

It is to be understood that where the silicon-containing compound used is a polymer, it is unnecessary to heat and mix the polymer and the thermoplastic resin in the presence of a free radical-releasing compound. Simple mixing above the softening point of the thermoplastic resin is sufficient.

According to the present technique, the thermoplastic resin modified with the silicon-containing compound is then molded into a predetermined shape. The shape of molding is not particularly limited and the molding may take a film, sheet, fiber, plate, rod, bar or another shape. The molding technique may be selected from conventional thermoplastic resin molding techniques depending on a particular shape of molding. One exemplary known technique is to pelletize the modified thermoplastic resin, heating the resin at or above its softening point, injecting the resin into a mold cavity, and cooling the resin below its softening point. Any desired molding machine such as injection molding and transfer molding machines may be used.

An integrated thermoplastic resin/silicone rubber article is obtained by integrating a molded shape of the modified thermoplastic resin with silicone rubber. Integration is accomplished by contacting an uncured silicone rubber with the molded thermoplastic resin, and curing the silicone rubber to the thermoplastic resin at a temperature below the softening point of the thermoplastic resin. The molding of thermoplastic resin may be either entirely or partially covered with the silicone rubber and the exact coverage depends on a particular application of the molding. Therefore, as the case may be, the molding may be entirely covered with the silicone rubber, the silicone rubber may be laid up on the molding in sheet form, or the silicone rubber may be molded or applied to a selected portion of the molding. More particularly, integration may be accomplished, for example, by applying an uncured silicone rubber to the thermoplastic resin molding as by coating or dipping and heating the coated molding to a temperature below the softening point of the thermoplastic resin for curing the silicone rubber. Another procedure involves laying up an uncured silicone rubber on the thermoplastic resin molding, heating and compressing the molding at a temperature below the softening point of the thermoplastic resin for curing the silicone rubber. An alternative procedure involves primary injection of the thermoplastic resin into a mold cavity by means of an injection molding machine to form a shape of the thermoplastic resin and secondary injection of an uncured silicone rubber into the cavity and around the shape.

The silicone rubber used herein is an addition reaction type silicone rubber composition. It may be in liquid, putty or paste form in uncured state, with the liquid or paste form generally designated as liquid silicone rubber being preferred for ease of molding.

One especially preferred example of the addition reaction type is a silicone rubber composition comprising (A) 100 parts by weight of a diorganopolysiloxane containing at least two alkenyl groups in a molecule and having a viscosity of 1 to 100 kg/ms (1,000 to 100,000 centipoise (cp)) at 25 °C, (B) an organohydrogenpolysiloxane having at least two hydrogen atoms attached to silicon atoms in a molecule in such an amount that the molar ratio (b/a) of silicon-attached hydrogen atoms (b mol) to alkenyl groups (a mol) in component (A) may range from 0.4 to 4, (C) 5 to 50 parts by weight of finely divided silica having a specific surface area of at least 50 m^2/g, and (D) a catalytic amount of a platinum compound or platinum series compound.

This composition will be described in further detail. Component (A) is an organopolysiloxane containing an alkenyl group in a molecule and having a viscosity of 1 to 100 kg/ms (1,000 to 100,000 cp) at 25°C. Preferably it is represented by the following general formula (1):

$$R^1_a SiO_{(4-a)/2} \qquad (1)$$

wherein R^1 which may be identical or different are independently selected from monovalent substituted and unsubstituted hydrocarbon groups having 1 to 10 carbon atoms, preferably 1 to 8 carbon atoms. Examples of the R^1 group include alkyl groups such as methyl, ethyl, propyl, butyl, hexyl and cyclohexyl groups; aryl groups such as phenyl, tolyl, xylyl and naphthyl groups; aralkyl groups such as benzyl and phenylethyl groups; and halo-substituted hydrocarbon groups such as chloromethyl and 3,3,3-trifluoropropyl groups. There should be present at least two alkenyl groups in a molecule on average. Among the substituents on the silicon atom, a vinyl group is typical of the alkenyl group, a methyl group is typical of the other substituent, and a trifluoropropyl group is desired where solvent resistance is required. Letter a is a number of from 1.9 to 2.4. This organopolysiloxane may be a linear one or a branched one containing $R^1SiO_{3/2}$ and $SiO_{4/2}$ units. It is preferred that the vinyl group be present at each end of the molecular chain.

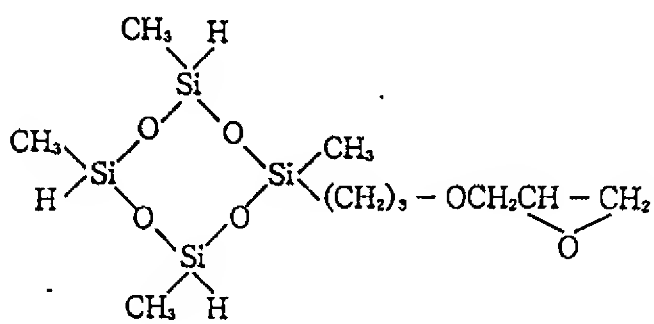
Component (B) is an organohydrogenpolysiloxane which serves as a cross linking agent by reacting with the alkenyl group-containing organopolysiloxane (A). Its molecular structure is not particularly limited and conventionally avail-

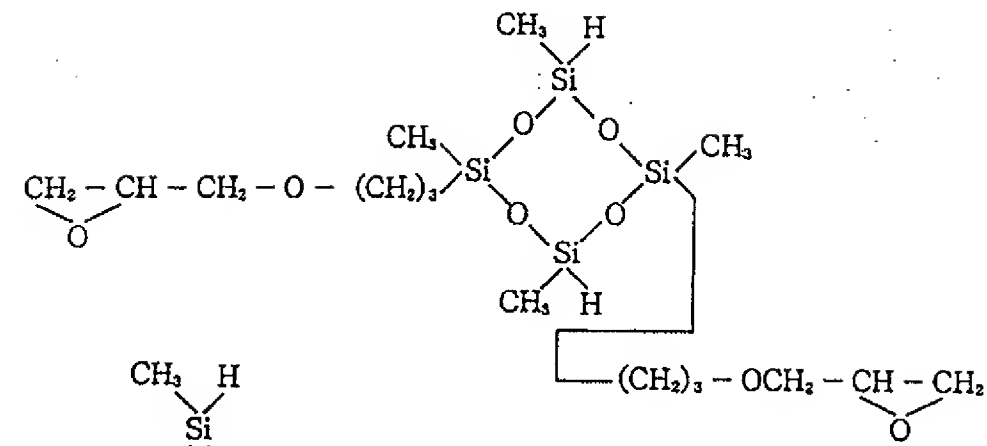
able ones including linear, cyclic and branched structures may be used. It should contain at least two hydrogen atoms attached to silicon atoms in a molecule. The substituents attached to silicon atom (other than the hydrogen atoms) may be the same as mentioned for R^1 in component (A). Component (B) is added in such an amount that the number of hydrogen atoms directly attached to silicon atoms in component (B) may range from 0.4 to 4 equivalents, especially from 0.8 to 2 equivalents per alkenyl group in the organopolysiloxane or component (A). With less than 0.4 equivalents of hydrogen atom, the cross-linking density may be too low and the cured silicone rubber would become less resistant against heat. Above 4 equivalents, foaming may occur through dehydrogenation reaction and heat resistance would be adversely affected. This organohydrogenpolysiloxane may be prepared by a conventional well-known procedure, for example, simply by equilibrating octamethylcyclotetrasiloxane and/or tetramethylcyclotetrasiloxane and a compound containing a $(CH_3)_3SiO_{1/2}$ unit or $H(CH_3)_2SiO_{1/2}$ unit forming a terminal group in the presence of a catalyst such as sulfuric acid, trifluoromethanesulfonic acid and methanesulfonic acid at a temperature of -10°C to +40°C.

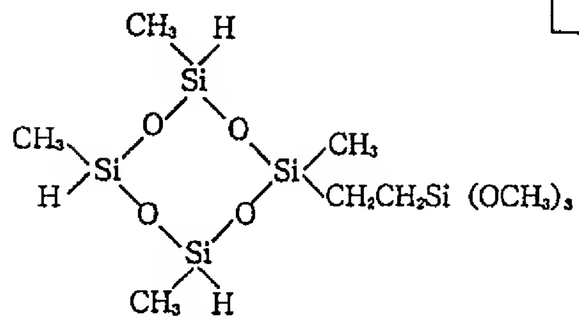
Component (C) is finely divided silica which is effective for imparting strength to an elastomer resulting from curing of the addition type silicone rubber composition. Since the silica is a reinforcing filler to the silicone rubber, it should have a specific surface area of at least 50 m^2/g. Examples of the finely divided silica include hydrophilic silica species, for example, such as Aerosil 130, 200 and 300 (Nippon Aerosil K.K. and De-Gussa), Cabosil MS-5 and MS-7 (Cabot Corp.), Rheolosil QS-102 and 103 (Tokuyama-Soda K.K.), and Nipsil LP (Nippon Silica K.K.); and hydrophobic silica species, for example, such as Aerosil R-812, R-812S, R-972 and R-974 (De-Gussa), Rheolosil MT-10 (Tokuyama-Soda K.K.), and Nipsil SS series (Nippon Silica K.K.). Note that Aerosil, Cabosil, Rheolosil and Nipsil are trade marks of the suppliers concerned. The silica is preferably blended in amounts of 5 to 50 parts, especially 10 to 40 parts by weight per 100 parts by weight of component (A) or organopolysiloxane.

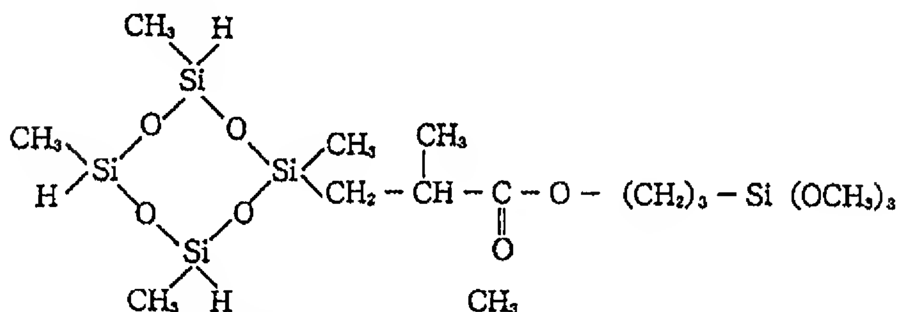
Component (D) is a platinum series catalyst for promoting addition reaction or hydrosilylation between components (A) and (B). The platinum catalyst may be selected from well-known ones, for example, platinum black, chloroplatinic acid, alcohol-modified chloroplatinic acid, and complexes of chloroplatinic acid with olefins, aldehydes, vinylsiloxanes or acetylene alcohol. The catalyst is added in a catalytic amount which may vary in accordance with the desired curing rate although it generally ranges from about 0.1 to about 1000 parts, preferably from about 1 to about 200 parts by weight of Pt per million parts by weight of component (A).

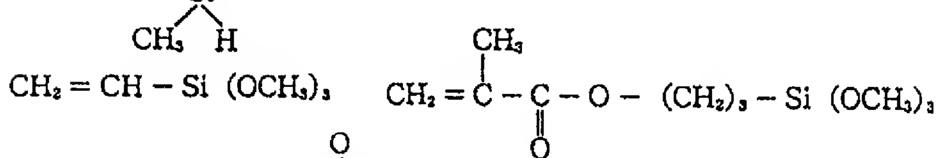
In order to further increase the bonding force between the addition type silicone rubber composition and the thermoplastic resin, an adhesion modifier is preferably added to the addition type silicone rubber composition. A typical adhesion modifier is a compound containing a hydrogen atom or aliphatic unsaturated group directly attached to a silicon atom and at least one group selected from the group consisting of an alkoxysilyl, oxirane and acid anhydride group. Examples of this compound are given below.

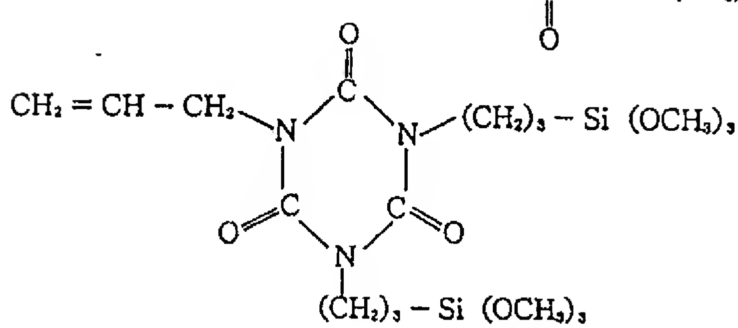












The adhesion modifier is added in amounts of 0 to 20 parts, preferably 0.5 to 10 parts by weight per 100 parts by weight of component (A) or organopolysiloxane. It is to be noted that where an adhesive modifier is added, the silicone rubber can adhere to a mold if used. It is then recommended to coat the mold with a release agent such as Teflon resin so that the silicone rubber may not adhere to the mold.

Further, if it is desired to adjust the curing time, one or more controlling agents may be used. Examples of control-

ling agents include vinyl-containing organopolysiloxanes such as vinylcyclotetrasiloxane, triallylisocyanurate, alkylmaleates, acetylene alcohols and their modified silanes and siloxanes, hydroperoxides, tetramethylethylenediamine and benzotriazole.

As means for increasing the mechanical strength of the silicone rubber composition without increasing the viscosity thereof, a silicone oil-soluble silicone resin comprised essentially of SiO_2 and $R^1_3\ SiO_{1/2}$ units wherein R^1 is as defined above and containing at least one alkenyl group in a molecule may be used instead of or in addition to component (C) or finely divided silica.

In addition to the above-mentioned components, the silicone rubber composition may further contain non-reinforcing fillers such as ground quartz, diatomaceous earth, and calcium carbonate, inorganic pigments such as cobalt blue, coloring agents such as organic dyes, and heat resistance/flame retardancy modifiers such as cerium oxide, zinc carbonate, manganese carbonate, red iron oxide, titanium oxide, and carbon black.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation. All parts are by weight.

Example 1

A Labo-Plasto mill (manufactured by Toyo Seiki K.K.) was charged with 100 parts of a polyethylene resin (low density polyethylene F101-3 manufactured by Sumitomo Chemical K.K.) and 5 parts of a silicon-containing compound of the following formula:

$$CH_2{=}CHC_6H_4Si(O\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}H)_3$$

They were mixed for 15 minutes at 180°C in a nitrogen atmosphere.

The modified resin was admitted into a compression mold coated with Teflon® resin and compressed into a sheet 2 mm thick. An addition curing type silicone rubber composition (KE 1940-40A/B manufactured by Shin-Etsu Chemical Industry Co., Ltd.) was admitted into the mold cavity having the sheet received therein, heat cured at 80°C for 5 minutes, and cooled down to room temperature. An integrally molded sheet was removed from the mold. Its dimensions were 2.5 mm x 10 mm x 4 mm thick, and it consisted of a silicone rubber layer 2 mm thick and a polyethylene resin layer 2 mm thick.

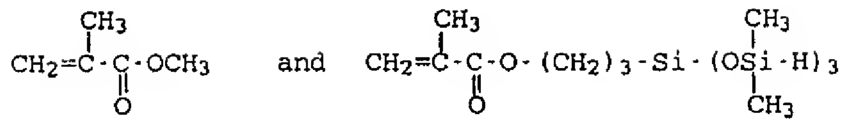
In the molded sheet, the silicone rubber layer and the polyethylene resin layer were integrally bonded. A 180°-peeling bond strength test on this sheet revealed a strong bond at the interface.

Example 2

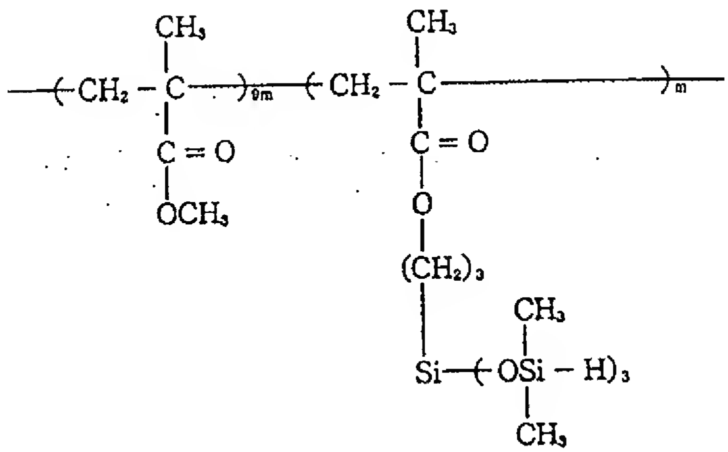
Example 1 was repeated except that a polypropylene resin (100% propylene polymer W101 manufactured by Sumitomo Chemical K.K.) was used instead of the polyethylene resin, and the resin and the silicon-containing compound were mixed for 15 minutes at 200°C in a nitrogen atmosphere. A sheet consisting of a silicone rubber layer and a polypropylene resin layer was integrally molded. A 180°-peeling bond strength test on this sheet revealed a strong bond at the interface.

Example 3

A Banbury mixer was charged with 100 parts of a polyamide resin (nylon-11 Benso P40TL manufactured by Toray K.K.) and 5 parts of a silicon-containing compound polymer defined below. They were mixed for 15 minutes at 210°C in a nitrogen atmosphere. The silicon-containing compound polymer was obtained by radical polymerization between



in a molar ratio of 9:1 in the presence of an azobisisobutyronitrile (AIBN) catalyst. The polymer is represented by the following formula:



(Letter m is a positive integer.)

As in Example 1, the modified resin was admitted into a compression mold coated with Teflon resin and compression molded into a sheet of 2 mm thick. An addition curing type silicone rubber composition was admitted into the mold cavity having the sheet received therein, heat cured at 80°C for 5 minutes, and cooled down to room temperature. An integrally molded sheet was removed from the mold.

In the molded sheet, the silicone rubber layer and the polyethylene resin layer were integrally bonded. A 180° -peeling bond strength test on this sheet revealed a strong bond at the interface.

There have been described integrated articles comprised of thermoplastic resins such as polyethylene, polypropylene and polyamide resins having silicon rubber firmly bonded thereto. The articles can be used in a variety of applications covering electric, electronic and automotive fields while taking advantage of the inherent reliability in heat resistance, weather resistance and electrical properties of the silicone rubber. The method described herein ensures that a firmly united thermoplastic resin/silicone rubber article is manufactured in a simple manner.

Claims

1. An integrated thermoplastic resin/silicone rubber article comprising

    (a) a moulded shape of a thermoplastic resin which has been modified by melt-mixing with a compatible monomeric or polymeric silicon-containing compound having per molecule at least one aliphatic unsaturated group and at least one $-SiR_2H$ or $-SiRH_2$ group, R being C_{1-10} hydrocarbon with optional substitution;
    and
    (b) a silicone rubber layer formed by curing, at a temperature below the softening point of the thermoplastic resin, an addition-curable silicone rubber composition in contact with the moulded shape.

2. An article according to claim 1 in which the thermoplastic resin is selected from polyethylene, polypropylene, fluorocarbon, polyamide and polycarbonate resins.

3. An article according to claim 1 or claim 2 in which the aliphatic unsaturated group in the silicon-containing com-

pound is selected from alkenyl, acryloxypropyl, methacryloxypropyl, cyclohexenyl, cyclopentadienyl, ethynyl and cinnamylpropyl groups.

4. An article according to any one of the preceding claims in which the silicon-containing compound is monomeric and the thermoplastic resin has been modified by free radical reaction with the monomeric silicon-containing compound.

5. An article according to any one of claims 1 to 3 in which the thermoplastic resin has been modified by simple mixing with the polymeric silicon-containing compound.

6. An article according to any one of the preceding claims in which the silicon-containing compound is of the formula

$$\begin{array}{ccccccc} & R & & R_a & & R & \\ & | & & | & & | & \\ RCH= & CH & -Q- & Si & -(O & SiH &)_{3-a} \\ & & & & & | & \\ & & & & & R & \end{array}$$

in which

Q is substituted or unsubstituted C_{1-10} hydrocarbon, or C_{1-10} $COOR^1$ where R^1 is substituted or unsubstituted hydrocarbon; R groups are selected from H and substituted and unsubstituted C_{1-8} hydrocarbon groups, and a is 0, 1 or 2.

7. An article according to claim 6 in which R^1 when present is alkylene or arylene and R groups are selected from H, C_{1-8} alkyl and C_{1-8} aryl.

8. An article according to any one of the preceding claims 1 to 3 and 5 in which the silicon-containing compound is a polymer of a compound of the formula

$$\begin{array}{ccccccc} & R & & R_a & & R & \\ & | & & | & & | & \\ RCH= & CH & -Q- & Si & -(O & SiH &)_{3-a} \\ & & & & & | & \\ & & & & & R & \end{array}$$

in which

Q is substituted or unsubstituted C_{1-10} hydrocarbon, or C_{1-10} $COOR^1$ where R^1 is substituted or unsubstituted hydrocarbon; R groups are selected from H and substituted and unsubstituted C_{1-8} hydrocarbon groups, and a is 0, 1 or 2,
or a copolymer thereof with another such compound or with an alkyl acrylate, styrene, maleic anhydride, vinyl ether, vinyl acetate or vinyl silane.

9. An article according to any one of the preceding claims in which the silicone rubber is obtainable by curing an addition-curable composition comprising

(A) 100 parts by weight of diorganopolysiloxane having at least two alkenyl groups per molecule and viscosity of from 1 to 100kg/ms at 25°C;
(B) organohydrogenpolysiloxane having at least two silicon-attached hydrogen atoms per molecule and present in such amount that the molar ratio (b/a) of the silicon-attached hydrogen atoms (b mol) to alkenyl groups (a mol) in component (A) is in the range 0.4 to 4;
(C) 5 to 50 parts by weight of finely-divided silica having a specific surface area of at least $50m^2/g$, and
(D) a catalytic amount of a platinum compound or platinum series compound.

10. A method of making a thermoplastic resin/silicone rubber integrated article comprising the steps of

(a) modifying a thermoplastic resin by melt-mixing and heating with it a compatible monomeric or polymeric silicon-containing compound having per molecule at least one aliphatic unsaturated group and at least one $-SiR_2H$ or $SiRH_2$ group, R being C_{1-10} hydrocarbon with optional substitution;
(b) moulding the modified thermoplastic resin into a shape;
(c) contacting an uncured addition-curable silicone rubber composition with the moulded thermoplastic resin, and
(d) addition-curing the silicone rubber onto the thermoplastic resin at a temperature below the softening point of the thermoplastic resin.

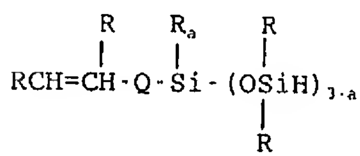
11. A method according to claim 10 in which the thermoplastic resin is selected from polyethylene, polypropylene, fluorocarbon, polyamide and polycarbonate resins.

12. A method according to claim 10 or claim 11 in which the aliphatic unsaturated group in the silicon-containing compound is selected from alkenyl, acryloxypropyl, methacryloxypropyl, cyclohexenyl, cyclopentadienyl, ethynyl and cinnamylpropyl groups.

13. A method according to any one of claims 10 to 12 in which a free radical releasing compound is mixed with the resin, and the silicon-containing compound is a monomer which in step (a) reacts with the thermoplastic resin by a free-radical mechanism.

14. A method according to any one of claims 10 to 12 in which the silicon-containing compound is a polymer simply melt-mixed with the thermoplastic resin.

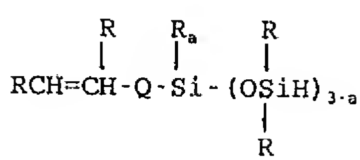
15. A method according to any one of claims 10 to 14 in which the silicon-containing compound is of the formula



in which

Q is a C_{1-10} substituted or unsubstituted hydrocarbon, or C_{1-10} $COOR^1$ where R^1 is substituted or unsubstituted hydrocarbon; R groups are selected from H and substituted and unsubstituted C_{1-8} hydrocarbon groups, and a is 0, 1 or 2.

16. A method according to any one of claims 10 to 12 and 14 in which the the silicon-containing compound is a polymer of a compound of the formula



in which

Q is a C_{1-10} substituted or unsubstituted hydrocarbon, or C_{1-10} $COOR^1$ where R^1 is substituted or unsubstituted hydrocarbon; R groups are selected from H and substituted and unsubstituted C_{1-8} hydrocarbon groups, and a is 0, 1 or 2,
or a copolymer thereof with another such compound or with an alkyl acrylate, styrene, maleic anhydride, vinyl

ether, vinyl acetate or vinyl silane.

17. A method according to any one of claims 10 to 16 in which the silicone rubber is obtainable by curing an addition-curable composition comprising

(A) 100 parts by weight of diorganopolysiloxane having at least two alkenyl groups per molecule and viscosity of from 1 to 100kg/ms at 25°C;
(B) organohydrogenpolysiloxane having at least two silicon-attached hydrogen atoms per molecule and present in such amount that the molar ratio (b/a) of the silicon-attached hydrogen atoms (b mol) to alkenyl groups (a mol) in component (A) is in the range 0.4 to 4;
(C) 5 to 50 parts by weight of finely-divided silica having a specific surface area of at least $50m^2/g$, and
(D) a catalytic amount of a platinum compound or platinum series compound.

Patentansprüche

1. Verbundgegenstand aus thermoplastischem Harz/Silikongummi, umfassend

(a) eine geformte Gestalt aus einem thermoplastischen Harz, das durch Schmelzvermischen mit einer verträglichen, monomeren oder polymeren, siliziumhältigen Verbindung modifiziert wurde, die pro Molekül zumindest eine aliphatische ungesättigte Gruppe und zumindest eine $-SiR_2H-$ oder $-SiRH_2$-Gruppe aufweist, wobei R ein gegebenenfalls substituierter C_{1-10}-Kohlenwasserstoff ist; und
(b) eine durch Härten einer additionshärtbaren Silikonkautschukzusammensetzung bei einer Temperatur unterhalb des Erweichungspunkts des thermoplastischen Harzes in Kontakt mit der geformten Gestalt gebildete Silikongummischicht.

2. Gegenstand nach Anspruch 1, bei dem das thermoplastische Harz aus Polyethylen-, Polypropylen-, Fluorkohlenwasserstoff-, Polyamid- und Polycarbonatharzen ausgewählt ist.

3. Gegenstand nach Anspruch 1 oder 2, bei dem die aliphatische ungesättigte Gruppe in der siliziumhältigen Verbindung aus Alkenyl-, Acryloxypropyl-, Methacryloxypropyl-, Cyclohexenyl-, Cyclopentadienyl-, Ethinyl- und Cinnamylpropylgruppen ausgewählt ist.

4. Gegenstand nach einem der vorangegangenen Ansprüche, bei dem die siliziumhältige Verbindung monomer ist und das thermoplastische Harz durch Radikalreaktion mit der monomeren siliziumhältigen Verbindung modifiziert ist.

5. Gegenstand nach einem der Ansprüche 1 bis 3, bei dem das thermoplastische Harz durch einfaches Vermischen mit der polymeren siliziumhältigen Verbindung modifiziert ist.

6. Gegenstand nach einem der vorangegangenen Ansprüche, bei dem die siliziumhältige Verbindung der Formel

$$\begin{array}{c}
R\quad R_a\quad\ \ R\phantom{)_{3-a}} \\
|\quad\ \ |\quad\ \ \ \ |\phantom{)_{3-a}} \\
RCH{=}CH\text{-}Q\text{-}Si\text{-}(OSiH)_{3-a} \\
|\phantom{H)_{3-a}} \\
R\phantom{H)_{3-a}}
\end{array}$$

entspricht, worin Q ein substituierter oder unsubstituierter C_{1-10}-Kohlenwasserstoff oder C_{1-10}-$COOR^1$ ist, worin R^1 ein substituierter oder unsubstituierter Kohlenwasserstoff ist; die Gruppen R aus H und substituierten und unsubstituierten C_{1-8}-Kohlenwasserstoffgruppen ausgewählt sind und a = 0, 1 oder 2 ist.

7. Gegenstand nach Anspruch 6, bei dem R^1, falls vorhanden, Alkylen oder Arylen ist und die Gruppen R aus H, C_{1-8}-Alkyl und C_{1-8}-Aryl ausgewählt sind.

8. Gegenstand nach einem der Ansprüche 1 bis 3 und 5, bei dem die siliziumhältige Verbindung ein Polymer aus einer Verbindung der Formel

$$\mathrm{RCH{=}\overset{R}{\overset{|}{C}}H{-}Q{-}\overset{R_a}{\overset{|}{Si}}{-}(O\overset{R}{\overset{|}{\underset{\underset{R}{|}}{Si}}}H)_{2-a}}$$

worin Q ein substituierter oder unsubstituierter C_{1-10}-Kohlenwasserstoff oder C_{1-10}-$COOR^1$ ist, worin R^1 ein substituierter oder unsubstituierter Kohlenwasserstoff ist; die Gruppen R aus H und substituierten und unsubstutierten C_{1-8}-Kohlenwasserstoffgruppen ausgewählt sind und a = 0, 1 oder 2 ist,

oder ein Copolymer davon mit einer weiteren derartigen Verbindung oder mit einem Alkylacrylat, Styrol, Maleinsäureanhydrid, Vinylether, Vinylacetat oder Vinylsilan ist.

9. Gegenstand nach einem der vorangegangenen Ansprüche, bei dem der Silikongummi durch Härten der additionshärtbaren Zusammensetzung erhältlich ist, die umfaßt:

   (A) 100 Gewichtsteile Diorganopolysiloxan mit zumindest zwei Alkenylgruppen pro Molekül und einer Viskosität bei 25°C von 1 bis 100 kg/ms;
   (B) Organohydrogenpolysiloxan mit zumindest zwei am Silizium hängenden Wasserstoffatomen pro Molekül, das in einer solchen Menge vorhanden ist, daß das Molverhältnis (b/a) zwischen den am Silizium hängenden Wasserstoffatomen (b Mol) und den Alkenylgruppen (a Mol) in Komponente (A) im Bereich von 0,4 bis 4 liegt;
   (C) 5 bis 50 Gewichtsteile feinteiliger Kieselsäure mit einer spezifischen Oberfläche von zumindest 50 m^2/g; und
   (D) eine katalytische Menge einer Platinverbindung oder einer Verbindung eines Metalls der Platinreihe.

10. Verfahren zur Herstellung eines Verbundgegenstands aus thermoplastischem Harz und Silikongummi, folgende Schritte umfassend:

   (a) Modifizieren eines thermoplastischen Harzes durch Schmelzvermischen und gemeinsames Erhitzen mit einer verträglichen, monomeren oder polymeren, siliziumhältigen Verbindung, die pro Molekül zumindest eine aliphatische ungesättigte Gruppe und zumindest eine $-SiR_2H$- oder $SiRH_2$-Gruppe aufweist, wobei R ein gegebenenfalls substituierter C_{1-10}-Kohlenwasserstoff ist;
   (b) Formen des modifizierten thermoplastischen Harzes zu einer Gestalt;
   (c) In-Kontakt-Bringen einer ungehärteten additionshärtbaren Silikonkautschukzusammensetzung mit dem geformten thermoplastischen Harz und
   (d) Additionsaufhärten des Silikonkautschuks auf das thermoplastische Harz bei einer Temperatur unterhalb des Erweichungspunkts des thermoplastischen Harzes.

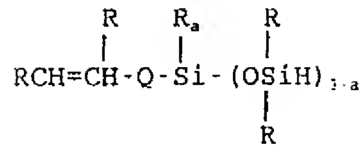
11. Verfahren nach Anspruch 10, bei dem das thermoplastische Harz aus Polyethylen-, Polypropylen-, Fluorkohlenwasserstoff-, Polyamid- und Polycarbonatharzen ausgewählt ist.

12. Verfahren nach Anspruch 10 oder 11, bei dem die aliphatische ungesättigte Gruppe in der siliziumhältigen Verbindung aus Alkenyl-, Acryloxypropyl-, Methacryloxypropyl-, Cyclohexenyl-, Cyclopentadienyl-, Ethinyl- und Cinnamylpropylgruppen ausgewählt ist.

13. Verfahren nach einem der Ansprüche 10 bis 12, bei dem eine freie Radikale freisetzende Verbindung mit dem Harz vermischt wird und die siliziumhältige Verbindung ein Monomer ist, das in Schritt (a) nach einem Radikalmechanismus mit dem thermoplastischen Harz reagiert.

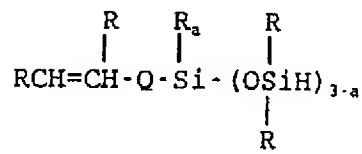
14. Verfahren nach einem der Ansprüche 10 bis 12, bei dem die siliziumhältige Verbindung ein einfach mit dem thermoplastischen Harz schmelzvermischtes Polymer ist.

15. Verfahren nach einem der Ansprüche 10 bis 14, bei dem die siliziumhältige Verbindung der Formel



entspricht, worin Q ein substituierter oder unsubstituierter C_{1-10}-Kohlenwasserstoff oder C_{1-10}-$COOR^1$ ist, worin R^1 ein substituierter oder unsubstituierter Kohlenwasserstoff ist; die Gruppen R aus H und substituierten und unsubstituierten C_{1-8}-Kohlenwasserstoffgruppen ausgewählt sind und a = 0, 1 oder 2 ist.

16. Verfahren nach einem der Ansprüche 10 bis 12 und 14, bei dem die siliziumhältige Verbindung ein Polymer aus einer Verbindung der Formel



worin Q ein substituierter oder unsubstituierter C_{1-10}-Kohlenwasserstoff oder C_{1-10}-$COOR^1$ ist, worin R^1 ein substituierter oder unsubstituierter Kohlenwasserstoff ist; die Gruppen R aus H und substituierten und unsubstituierten C_{1-8}-Kohlenwasserstoffgruppen ausgewählt sind und a = 0, 1 oder 2 ist,

oder ein Copolymer davon mit einer weiteren derartigen Verbindung oder mit einem Alkylacrylat, Styrol, Maleinsäureanhydrid, Vinylether, Vinylacetat oder Vinylsilan ist.

17. Verfahren nach einem der Ansprüche 10 bis 16, bei dem der Silikongummi durch Härten einer additionshärtbaren Zusammensetzung erhältlich ist, die umfaßt:

(A) 100 Gewichtsteile Diorganopolysiloxan mit zumindest zwei Alkenylgruppen pro Molekül und einer Viskosität bei 25°C von 1 bis 100 kg/ms;
(B) Organohydrogenpolysiloxan mit zumindest zwei am Silizium hängenden Wasserstoffatomen pro Molekül, das in einer solchen Menge vorhanden ist, daß das Molverhältnis (b/a) zwischen den am Silizium hängenden Wasserstoffatomen (b Mol) und den Alkenylgruppen (a Mol) in Komponente (A) im Bereich von 0,4 bis 4 liegt;
(C) 5 bis 50 Gewichtsteile feinteiliger Kieselsäure mit einer spezifischen Oberfläche von zumindest 50 m^2/g und
(D) eine katalytische Menge einer Platinverbindung oder einer Verbindung eines Metalls der Platinreihe.

Revendications

1. Objet intégré en résine thermoplastique/caoutchouc de silicone comprenant

(a) une forme moulée d'une résine thermoplastique qui a été modifiée par mélange en phase fondue avec un composé contenant de la silicone monomère ou polymère compatible ayant, par molécule au moins un groupe aliphatique insaturé et au moins un groupe $-SiR_2H$ ou $-SiRH_2$, R étant un hydrocarbure C_{1-10} avec substitution facultative; et
(b) une couche d'un caoutchouc de silicone formée en durcissant, à une température en dessous du point d'amollissement de la résine thermoplastique, une composition d'un caoutchouc de silicone durcissable par addition en contact avec la forme moulée.

2. Objet selon la revendication 1, dans lequel la résine thermoplastique est sélectionnée parmi des résines de polyéthylène, de polypropylène, de fluorocarbone, de polyamide et de polycarbonate.

3. Article selon la revendication 1 ou la revendication 2, dans lequel le groupe aliphatique insaturé dans le composé

contenant de la silicone est sélectionné parmi les groupes alcényle, acryloxypropyle, méthacryloxypropyle, cyclohexényle, cyclopentadiényle, éthynyle et cinnamylpropyle.

4. Objet selon l'une quelconque des revendications précédentes, dans lequel le composé contenant de la silicone est monomère et la résine thermoplastique a été modifiée par réaction de radicaux libres avec le composé contenant de la silicone monomère.

5. Objet selon l'une quelconque des revendications 1 à 3, dans lequel la résine thermoplastique a été modifiée par simple mélange avec le composé contenant de la silicone polymère.

6. Objet selon l'une quelconque des revendications précédentes, dans lequel le composé contenant de la silicone est de la formule

$$RCH{=}\overset{\displaystyle R}{\overset{|}{C}}H{-}Q{-}\overset{\displaystyle R_a}{\overset{|}{S}}i{-}(O\overset{\displaystyle R}{\overset{|}{\underset{\underset{\displaystyle R}{|}}{S}}}iH)_{3-a}$$

dans laquelle

Q est hydrocarbure C_{1-10} substitué ou non substitué ou bien $COOR^1$ C_{1-10} où R^1 est hydrocarbure substitué ou non substitué; les groupes R sont sélectionnés parmi H et des groupes hydrocarbures C_{1-8} substitués et non substitués; et a est 0, 1 ou 2.

7. Article selon la revendication 6 dans lequel R^1, quand il est présent, est alkylène ou arylène et les groupes R sont sélectionnés parmi H, alkyle C_{1-8} et aryle C_{1-8}.

8. Objet selon l'une quelconque des revendications 1 à 3 et 5, dans lequel le composé contenant de la silicone est un polymère d'un composé de la formule

$$RCH{=}\overset{\displaystyle R}{\overset{|}{C}}H{-}Q{-}\overset{\displaystyle R_a}{\overset{|}{S}}i{-}(O\overset{\displaystyle R}{\overset{|}{\underset{\underset{\displaystyle R}{|}}{S}}}iH)_{3-a}$$

dans laquelle

Q est hydrocarbure C_{1-10} substitué ou non substitué ou bien $COOR^1$ C_{1-10} où R^1 est hydrocarbure substitué ou non substitué; les groupes R sont sélectionnés parmi H et des groupes hydrocarbures C_{1-8} substitués et non substitués, et a est 0, 1 ou 2,

ou leur copolymère avec un autre tel composé ou avec un acrylate d'alkyle, du styrène, de l'anhydride maléique, du vinyl éther, de l'acétate de vinyle ou du vinyl silane.

9. Objet selon l'une quelconque des revendications précédentes, dans lequel le caoutchouc de silicone peut être obtenu par durcissement d'une composition durcissable par addition comprenant

(A) 100 parties en poids d'un diorganopolysiloxane ayant au moins deux groupes alcényles par molécule et une viscosité de 1 à 100 kg/ms à 25°C;
(B) un organohydrogénopolysiloxane ayant au moins deux atomes d'hydrogène attachés à la silicone par molécule et présent en une quantité telle que le rapport molaire (b/a) des atomes d'hydrogène attachés à la silicone (b moles) aux groupes alcényles (a moles) dans le composant (A) soit de l'ordre de 0,4 à 4;
(C) 5 à 50 parties en poids de silice finement divisée ayant une aire superficielle spécifique d'au mois 50 m2/g, et

(D) une quantité catalytique d'un composé de platine ou d'un composé de la série platine.

10. Méthode de fabrication d'un objet intégré en résine thermoplastique/caoutchouc de silicone, comprenant les étapes de :

(a) modifier une résine thermoplastique par mélange en phase fondue et chauffage avec elle d'un composé contenant de la silicone monomère ou polymère compatible, ayant, par molécule, au moins un groupe aliphatique insaturé et au moins un groupe $-SiR_2H$ ou $SiRH_2$, R étant un hydrocarbure C_{1-10} avec substitution facultative;
(b) mouler la résine thermoplastique modifiée en une forme;
(c) mettre une composition d'un caoutchouc de silicone durcissable par addition non durci en contact avec la résine thermoplastique moulée, et
(d) durcir par addition le caoutchouc de silicone sur la résine thermoplastique à une température en dessous du point d'amollissement de la résine thermoplastique.

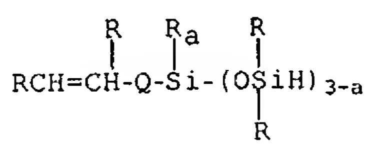
11. Méthode selon la revendication 10, dans laquelle la résine thermoplastique est sélectionnée parmi des résines de polyéthylène, de polypropylène, de fluorocarbone, de polyamide et de polycarbonate.

12. Méthode selon la revendication 10 ou la revendication 11, dans laquelle le groupe aliphatique insaturé dans le composé contenant de la silicone est sélectionné parmi les groupes alcényle, acryloxypropyle, méthacryloxypropyle, cyclohexényle, cyclopentadiényle, éthynyle et cinnamylpropyle.

13. Méthode selon l'une quelconque des revendications 10 à 12 dans laquelle un composé libérant des radicaux libres est mélangé à la résine, et le composé contenant de la silicone est un monomère qui, a l'étape (a), réagit avec la résine thermoplastique par un mécanisme de radicaux libres.

14. Méthode selon l'une quelconque des revendications 10 à 12, dans laquelle le composé contenant de la silicone est un polymère simplement mélangé en phase fondue avec la résine thermoplastique.

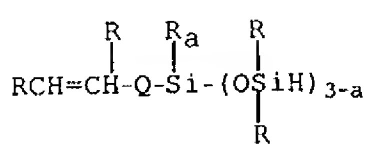
15. Méthode selon l'une quelconque des revendications 10 à 14 dans laquelle le composé contenant de la silicone est de la formule



dans laquelle

Q est un hydrocarbure C_{1-10} substitué ou non substitué ou bien $COOR^1$ C_{1-10} où R^1 est un hydrocarbure substitué ou non substitué; les groupes R sont sélectionnés parmi H et les groupes hydrocarbures C_{1-8} substitués et non substitués, et a est 0, 1 ou 2.

16. Méthode selon l'une quelconque des revendications 10 à 12 et 14, dans laquelle le composé contenant de la silicone est un polymère d'un composé de la formule



dans laquelle

Q est un hydrocarbure C_{1-10} substitué ou non substitué, ou bien $COOR^1$ C_{1-10} où R^1 est hydrocarbure substitué ou non substitué; les groupes R sont sélectionnés parmi H et des groupes hydrocarbures C_{1-8} substitués et non substitués et a est 0, 1 ou 2,

ou leur copolymère avec un autre tel composé ou avec un acrylate d'alkyle, du styrène, de l'anhydride maléique, du vinyl éther, de l'acétate de vinyle ou du vinyl silane.

17. Méthode selon l'une quelconque des revendications 10 à 16, dans laquelle le caoutchouc de silicone peut être obtenu par durcissement d'une composition durcissable par addition comprenant

(A) 100 parties en poids d'un diorganopolysiloxane ayant au moins deux groupes alcényles par molécule et une viscosité de 1 à 100 kg/ms à 25°C;
(B) un organohydrogénopolysiloxane ayant au moins deux atomes d'hydrogène attachés à la silicone par molécule et présents en une quantité telle que le rapport molaire (b/a) des atomes d'hydrogène attachés à la silicone (b moles) aux groupes alcényles (a moles) dans le composant (A) soit de l'ordre de 0,4 à 4;
(C) 5 à 50 parties en poids de silice finement divisée ayant une aire superficielle spécifique d'au moins 50m2/g, et
(D) une quantité catalytique d'un composé de platine ou d'un composé de la série platine.